The Analysis of Dioxin Using a Benchtop Mass Spectrometer

Application

6890/5973 Gas Chromatograph/Mass Selective Detector

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Abstract

Currently the analysis of dioxins uses high resolution mass spectrometry, (HRMS); often considered a prohibitively expensive technique. To move to a more cost-effective approach, improvements in the analytical method (sample cleanup and chromatographic separation) as well as improvements in sensitivity of benchtop mass spectrometers were needed.[1, 2]

Compared to earlier generations of benchtop mass spectrometers, the 5973 mass selective detector offers measurably greater sensitivity for electron-impact-based detection due to a number of innovative enhancements.[3]

Analysis via the GC/MSD System

This work focused on determining the detection limit for 2,3,7,8-tetrachlorodibenzo-p-dioxin with a GC/MSD system configured as outlined in this note. The desired analytical goal was to detect 0.2 pg.

A submitted sample [5 pg/µL (ppb); 2,3,7,8-TCDD in 95/5 hexane/ether] was diluted by a factor of 100 with pure hexane. (The hexane was analyzed for response at the appropriate masses prior to use to verify its purity with respect to this analyte.)

For both concentrations, the mass ratio 319.9/321.9 was measured to confirm appropriate isotopic performance. Moreover, the response factors for m/z = 321.9 were determined for both levels and compared to verify linearity over a large concentration range.

Results

The mass ratio of 319.9/321.9 is 78%, correctly reflecting appropriate isotopic abundances. Comparing the response ratios of 0.05 pg and 5 pg injections (1 µL each level), we observed that those were nearly equal: 24.6 and 23.0 (2302.6 ÷ 100).

The signal/noise for the 0.05 pg injection is about 4:1 peak/peak, representing an approximate detection limit on the system used.

The conclusion is that the sensitivity of a 5973 MSD operating as an electron impact instrument is well-suited to trace analysis of dioxins, making it a cost-effective instrument for use in EPA Methods 625 and 613.[4] For 2,3,7,8-TCDD, the detection limit with the 5973 is comparable to using HRMS. Note, however, that the ultimate method detection limits will depend on other factors — e.g., the sample matrix, type of sample cleanup used, etc. Additional sensitivity may be possible by using large volume injection techniques.[3] Future experiments will aim at evaluating the NCI (negative chemical ionization) performance of the 5973 for further gains in sensitivity and selectivity.

This will mean that a laboratory manager can choose configurations of both the chromatograph and the MSD to best match the needs of a laboratory workload. The work on the system described here demonstrated greatly enhanced sensitivity provided by cost-effective benchtop mass spectrometry.

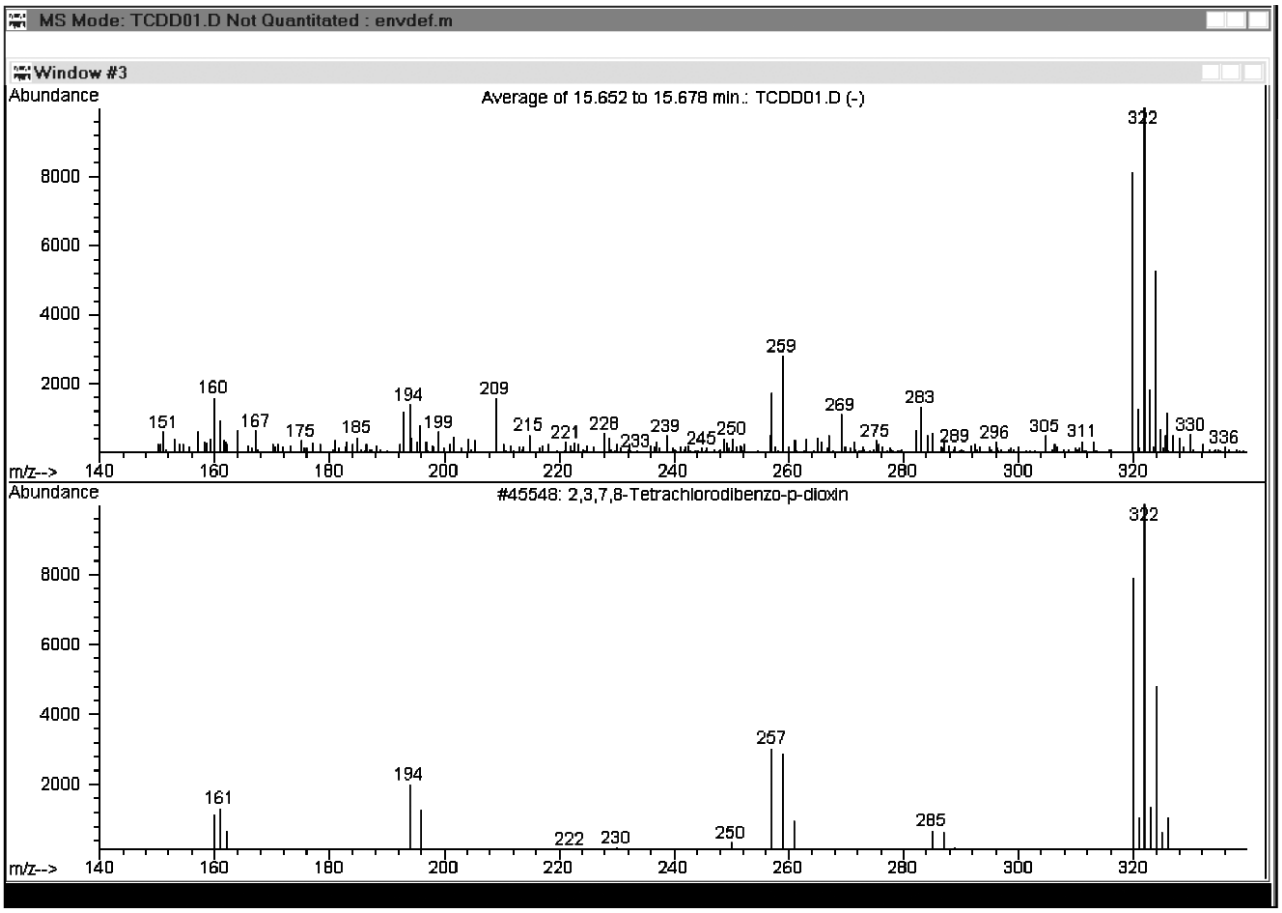

Figure 1. The match of the spectum for 5 pg 2,3,7,8-tetrachlorodibenzo-p-dioxin with the library search (lower panel). The match quality was 90%.

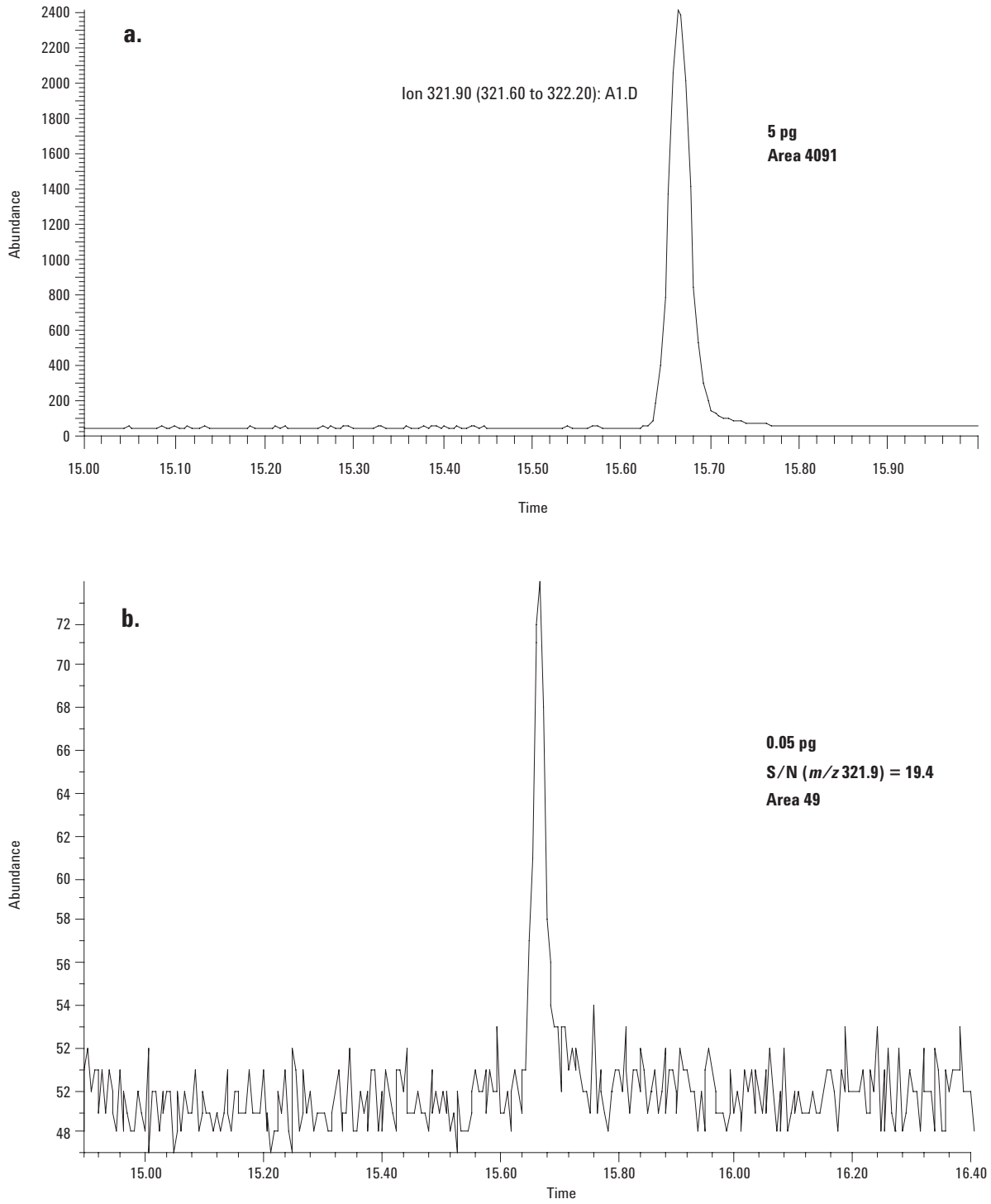

Figure 2. The TIC at *m/z* 321.9 for injection quantities of 5 pg (a.) and 0.05 pg (b.) in SIM mode.

6890 with 5973 MSD

Injection	• Pulsed splitless single taper liner with glass wool plug, P/N 5062-3587. • 250 °C • 1 µL injection volume • Viscosity delay, 1 sec • Sample washes, 3; post-injection solvent washes, 4
Column	HP-5MS: 30 m × 250 µm, 0.25 µm film (crosslinked 5% Ph Me Siloxane), P/N 19091S-433
Carrier	Helium, 37 cm/sec; vacuum compensation, on.
Temperature	Initial: 70 °C for 1.50 min
Program	Rate 1: 25.00 °C/min to 150 °C Rate 2: 10.00 °C/min to 280 °C Final: 280 °C for 0.00 min
Pressure	25.0 psi for 1.50 min; then
Program	1.0 mL/min constant flow rate
MSD	• Temperatures Transfer line = 300 °C Source = 230 °C Quadrupole = 106 °C • Tune = autotune • Emission current = 35 µamp • SIM mode, EMV = Autotune + 400 V • Solvent delay = 14.00 min • Dwell per ion = 125 msec • SIM Ions (*m/z*): 319.9, 321.9
Autosampler	7673B
ChemStation	G1701AA

References

1. P. R. Gardinali et al, Chemosphere 32 (1), pp. 1-11 (1996).
2. R. Malisch et al, Chemosphere 32 (1), pp. 31-44 (1996).
3. L. Doherty, "Enhancing Pesticide Analysis with a Highly Sensitive GC/MSD System," Application Note, Pub. No. (23) 5966-0370E (1997).
4. Code of Federal Regulations, Title 40, Vol. 13, Parts 136-149, Appendix A. Revised, July 1, 1997. U.S. Government Printing Office (via GPO Access; CITE: 40CFR136). Method 613 - 2,3,7,8-tetrachloro-dibenzo-p-dioxin by GC/MS (SIM). Method 625 - Base/Neutrals and Acids, Semivolatiles by GC/MS (SCAN).

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